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**(54) Decorative anodised films on
substrates**

(57) The films are produced by
depositing an anodisable coating (e.g.
Ta, Ti, Zr, alloys thereof and nitrides)
onto a substrate (e.g. stainless and
mild steel) by sputter ion plating
followed by anodising at a controlled
voltage in order to control oxide film

thickness and hence colour. Anodising
is known to generate a thin film on an
anodisable material. A particular film
thickness may generate a distinctive
interference colour if the oxide has a
high refractive index. However, not all
materials are anodisable and this
technique enables the properties of
anodisable films to be made more
generally available.

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SPECIFICATION

Anodised Films on Substrates

This invention relates to the provision of anodised coatings on substrates, for example, for decorative purposes.

5 Anodising is a well-known process in which a thin oxide film (e.g. of a few hundred Å thickness or greater) may be formed. A particular film thickness may generate a bright, distinctive interference colour if the oxide is of high refractive index. This, however, has limited applicability since not all materials will anodise satisfactorily. Thus, many materials have low corrosion potentials and will only form very thin oxide films at very low voltages before the films break down and the material corrodes. We have now
10 devised a way of making the properties of anodised films more generally applicable.

Thus, according to the present invention a method of providing a substrate with an anodised oxide film comprises the steps of

- (i) depositing an anodisable coating on the substrate by means of sputter ion plating; and
- 15 (ii) anodising the coating to produce an oxide film, wherein the anodising voltage is controlled in order to control the thickness of the film. 15

We have been able to control the thickness of the oxide film reproducibly and uniformly to give, in cases where the oxide has a high refractive index, a variety of colours. Also, we have been able to apply our method to a variety of substrates, including substrates which cannot readily be anodised and which may be relatively inexpensive and easy to fabricate.

20 An important feature of our invention is the use of Sputter Ion Plating in step (i) since this enables a high quality coating of uniform thickness and good adhesion to be obtained, which is required for the anodising step. Thus, the coating should be dense and free from voids, porosity, and cracks which may lead to corrosion of the substrate during subsequent anodising. Sputter Ion Plating is a coating technique where material is transferred from a cathode to a substrate in the presence of a DC glow
25 discharge in a soft vacuum chamber and where material is generated from the cathode by the action of ion bombardment, i.e. sputtering, and ultimately diffuses to the substrate. Sputter Ion Plating is described in detail in a number of references in the art, for example, "Wire Industry", 44, December 1977, pages 771 to 777; Welding Institute Reprint, Advances in Surface Coating Technology ~ International Conference, London 13—15 February 1978, pages 53—59; Proceedings of 'IPAT'
30 Conference, Edinburgh (June 1977) ps. 177—186. 30

Step (ii) may be carried out by methods known in the art. When the oxide film is insulating and fully formed, the anodising current should drop to zero. However, further anodising may be carried out on the same sample, but at a higher voltage since the oxide film is only insulating at voltages up to the voltages at which it was formed. A higher voltage breaks down the film until it has grown to a sufficient
35 thickness to be insulating again. Thus, repeated anodising at greater and greater voltages can produce a multi-coloured sample. Also, insulating materials such as paint, silicone grease and "Letraset" coverings etc. may be used to mask off areas whilst anodising to achieve a background colour; the masking material may then be removed and anodising carried out at a different voltage to give a two-tone effect. A simple extension of this procedure may be carried out to obtain a multi-tone effect.

40 The present invention may be applied to metallic or to non-metallic (e.g. ceramic) substrates. Examples of metallic substrates are mild, carbon and stainless steels; Al and Al alloys; Ta; Cu; Mo and Ni. Examples of non-metallic substrates are Al_2O_3 , porcelain and glass.

The anodisable coating may be of materials which are known to anodise such as Nb, Ti, Ta, Zr and also alloys of these elements. The coating may be a nitride coating such as TiN, ZrN, TiZrN, deposited by
45 carrying out the sputter ion plating in a reactive environment (e.g. containing N_2). When anodised, such nitride coatings exhibit distinctive colours in comparison with colours obtained by anodising the corresponding element. 45

The coatings may have a range of thickness. For example, we have made coatings with thicknesses from 0.1 μm to 180 μm .

50 Whilst the main purpose of our invention is to provide coatings for decorative purposes, coatings may be produced which have application in other areas such as constituting insulating layers for capacitors and microcircuitry. 50

The invention will now be particularly described, by way of example only, as follows.

GENERAL PROCEDURE

55 *Sputter Ion Plating* 55

An apparatus as described in the abovementioned prior art references was used. A coating vessel consists of a resistance heated stainless steel inner chamber, at the walls of which are suspended a series of target plates constituting the coating material. The substrate to be coated is suspended at the centre of the chamber.

60 The chamber was pumped down to 10—100 m.torr pressure with a flowing argon atmosphere of high purity. The argon had been purified by passing over freshly deposited titanium. The chamber was 60

heated to a temperature of around 300/350°C by which stage outgassing of the substrate and target and evaporation of organic material has occurred. Further cleaning in some circumstances was achieved by applying a high negative voltage (1000 V) for about $\frac{1}{2}$ hour onto the substrate causing an argon glow discharge to be set up with ion bombardment causing removal of surface atoms on the substrate.

- 5 A high negative voltage (400—1000 V) was then applied to the targets to produce a glow discharge with net transfer of material from the targets onto the substrate, i.e. coating of the substrate by deposition. The coating was carried out at 200—350°C; no external heating was required since the above process generates sufficient power to maintain this temperature. 5

- 10 If desired, a negative bias of 20—150 V may be applied to the coated substrate causing densification of the coating by resputtering of deposited material and ion polishing. 10

- The above produces a coating of an element or an alloy. If it is desired to deposit a nitride coating, this can be done by admitting nitrogen at a small partial pressure (1—100 m torr) into the chamber during the deposition process. This causes a distinct change in the glow discharge characteristics and generally reduces the rate of deposition, though it does allow very hard, coloured nitride coatings to be deposited. 15

The deposition rates may vary from 0.5 $\mu\text{m}/\text{hour}$ to 10 $\mu\text{m}/\text{hour}$ according to power density, though, as stated above, rates are lower when nitrogen is introduced.

Anodising

- 20 This was carried out by using an electrolytic bath contained in a glass vessel, a power supply unit (e.g. of 0.110 V and 0—3 A output or more) with current and voltage readout, and a non-corroding cathode (e.g. of Ta or stainless steel) immersed in the bath. The solution used in the bath may, for example, be 1% by weight KOH in water, or ammonium diborate solution made up to pH9 by addition of ammonia solution. 20

- 25 The sputter ion plated substrate was carefully cleaned and connected up as the anode and immersed, either wholly or partly into the bath. A voltage known to give a particular colour was applied. When the resulting oxide film was fully formed, the current fell to zero. The power supply unit was switched off, the coated substrate removed and washed in water and solvent. If desired, further anodising may be carried out at successively higher voltages to give different colours. 25

SPECIFIC PROCEDURES

- 30 *Sputter Ion Plating* 30

- A number of substrates were coated with metals and binary alloys at pressures of between 15 and 25 m torr. Typical target power densities ranged from 1.78 kW/m^2 for Ti to 5.08 kW/m^2 for Zr. Typical substrate power densities were 0.41 kW/m^2 to 1.18 kW/m^2 . These power levels ensured deposition of the coating at chamber temperatures of between 200°C and 300°C. Higher or lower power levels may be used as required. The coating process time was usually 1 to 15 hours. 35

- Nitrides were usually deposited as follows. A simple metal coating was deposited for about $\frac{1}{2}$ hour at power levels as indicated above and at pressures of 20 to 25 m torr. The getter was switched off and nitrogen admitted at a partial pressure of 1—10 m torr. The power levels typically increased by 10% at the targets, because of the different discharge conditions, but at the substrate the power density generally dropped by 40—70%. In the extreme case of ZrN, the target power density increased by 12%, though the substrate power density only decreased by 60%. For all the nitride coatings, the temperature in the chamber was maintained by process heat at 200 to 300°C and the total process time was typically $1\frac{1}{2}$ to 3 hours. The initial metal coating may be omitted if desired. 40

Anodising

- 45 The above coated substrates were anodised in accordance with the general anodising procedure. We found that Al coatings anodised best in a borate bath whilst other metals, alloys and nitrides could be anodised in either bath, though nitride coatings were found to anodise more quickly in a borate bath. The results are summarised in the table below which is in two parts and shows the colours achieved and the specific voltage at which they were achieved with a specified voltage range. 45

ANODISING VOLTAGE RANGE (V)

Coating	0-10	11-20	21-30	31-40	31-40	Substrates
Ti	10V mustard	20V mid-blue	30V pale blue	40V yellow/green		Al alloy, Ta C. Steel, Stainless Steel, glass
Ta		20V, 22V dark blue → mauve	30V grey/blue 35V blue	40V ice blue	50V ice yellow → pale green	Mo, Stainless Steel, Mild Steel, Al alloy glass, steatite Al ₂ O ₃
Zr	10V mustard	15V purple 20V blue	30V ice blue	40V yellow	45V yellow	Ta, Al alloy
Nb	10V brown	15V dark blue 20V grey/blue	30V colourless	40V yellow	50V mauve → purple	Stainless Steel, Ni
Al	20-110V dark grey → light grey with thicker oxide formation					Ta, Stainless Steel
TiZr	10V mustard	15V purple 20V mid-blue	30V ice blue	35V yellow/ colourless 40V light yellow	50V yellow	Ta, Mild Steel
TiTa	10V grey/ mustard	20V mid-blue	30V grey/blue	34V ice blue 40V ice yellow	50V yellow	Al alloy, Ta
TiN	10V brown	20V light yellow → white	31V dull yellow/white	40V white		Stainless Steel, Ta

ANODISING VOLTAGE RANGE (V)

Coating	0-10	11-20	21-30	31-40	41-50	Substrates
ZrN	10V dull brown		30V mid brown		50V white film	Stainless Steel
AlN		20V brown	25V mid-blue	40V grey/blue		Ta, Stainless Steel
TiZrN		20V brown → purple	27V, 30V grey/blue	35V grey → ice blue 40V ice blue → ice yellow	45V yellow 50V pale green → gold	Cu, Al, Ni, Stainless Steel
TiTaN	10V brown	15V dark brown 20V blue	25V blue 30V yellow → pale blue	35V ice blue 40V yellow	51V orange	Ta, C. Steel Al, Stainless Steel

ANODISING VOLTAGE RANGE (V)

Coating	51-60	61-70	71-80	81-90	91-100	Substrates
Ti	60V red/mauve					Al alloy, Ta C. Steel, Stainless Steel, glass
Ta	60V yellow	70V orange → purple	80V mid blue → purple	90V green → turquoise	100V green 110V pink	Mo, Stainless Steel, Al alloy, glass, steatite, Al ₂ O ₃
Zr	51V purple	62V turquoise → peacock blue 70V green	75V yellow/green 80V orange → purple	90V purple	95V red/mauve 101V dark green 110V light green	Ta, Al alloy
Nb	60V turquoise	70V lime green	80V lilac	90V mauve	105V green	Stainless Steel
Al	20 - 110 dark grey → light grey with thicker oxide formation					Ta, Stainless Steel
TiZr	60V purple	70V sea green	75V green 80V yellow/green	90V pink → lime	105V red/purple	Ta, Mild Steel
TiTa	60V pink/lilac	70V vivid blue	75V turquoise 80V lime	90V gold	100V pink 110V mauve	Al alloy, Ta
TiN	60, 62V v. thick white oxide					Stainless Steel, Ta
ZrN		70V thick white oxide				Stainless Steel

ANODISING VOLTAGE RANGE (V)

Coating	51-60	61-70	71-80	81-90	91-110	Substrates
AlN	60V ice blue		80V ice/white	85V white		Ta, Stainless Steel
TiZrN	56V yellow	70V crimson → pink				Cu, Al, Ni, Stainless Steel
TiTaN	60V orange/brown	70V green/tan	80V maroon/lilac	90V mauve	105V lilac	Ta, C. Steel Al, Stainless Steel

CLAIMS

1. A method of providing a substrate with an anodised oxide film which comprises the steps of
 - (i) depositing an anodisable coating on the substrate by means of sputter ion plating; and
 - (ii) anodising the coating to produce an oxide film, wherein the anodising voltage is controlled in order to control the thickness of the film.
2. A method according to claim 1 wherein the substrate is metallic.
3. A method according to claim 2 wherein the metallic substrate is a steel.
4. A method according to claim 2 wherein the metallic substrate is aluminium or an alloy thereof.
5. A method according to claim 1 the substrate is non-metallic.
6. A method according to claim 5 wherein the non-metallic substrate is a ceramic.
7. A method according to any one of the preceding claims wherein the coating has a thickness in the range from 0.1 μm to 180 μm .
8. A method according to any of the preceding claims wherein the coating comprises the elements Nb, Ti, Ta or Zr or an alloy of any of the said elements.
9. A method according to any of claims 1 to 7 wherein step (i) is carried out in a reactive environment for depositing a nitride coating on the substrate.
10. A method according to any of the preceding claims wherein anodising is carried out at a first voltage to produce an insulating oxide film and then at one or more subsequent voltages, the or each voltage to produce an insulating oxide film, wherein each voltage is greater than the voltage immediately preceding, thereby to produce an oxide film of variable thickness.
11. A method according to any of the preceding claims wherein part of the substrate carries a removable insulating material whilst anodising is carried out.
12. A method providing a substrate with an anodised oxide film substantially as described herein with reference to any one of the examples.
13. A substrate provided with an anodised oxide film by a method according to any of the preceding claims.